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EFFECT OF FORMATION CONDITIONS ON CATALYTIC PROPERTIES OF SELF-PURIFYING COATINGS

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It is found that the technological conditions for the formation of self-purifying coating depend on the sintering interval of the vitreous phase and its dispersion. The most porous coating with the maximum effect of self-purification (96 – 98%) was obtained on introducing 12 – 14 parts by weight of sodium silicate solution into the coating slip. The optimum coating structure provides for decomposition of food fats after multiple thermal cycling.

A self-purifying catalytic coating for decomposition of residual food fats on the walls of household utensils intended for cooking is a composite coating that contains a low-melting vitreous binder and catalysts of decomposition and oxidation of fats, i.e., oxides of variable-valence metals (Cr_2O_3 , CuO , MnO_2 , Co_2O_3 , etc.).

We earlier [1] investigated the effect of variable-valence metal oxides on the catalytic activity of a self-purifying coating. However, the catalytic activity also depends on the macrostructure of the coating, which can be controlled using several technological factors.

The present study is dedicated to studying the effect of the conditions of formation of self-purifying coatings on their service properties.

The main stages in the production of coatings include the synthesis of a low-melting vitreous binder, its milling to a certain fraction, activation of the catalyst, and thorough mixing together with refractory clay, sodium silicate solution (water glass), and electrolytes. The resulting slip is deposited on a steel substrate covered with an undercoat, dried, and fired at the optimum temperature.

The capacity of the coating to decompose residual food fats is due primarily to the chemical composition of the catalyst and the vitreous binder and a corresponding porous structure that ensures maximum surface area of contact of the food fats with the catalyst.

The catalytic activity of the coating was estimated based on the self-purification coefficient K_s , which was determined based on the weight loss Δm in drops of Brolio vegetal fat by exposing the sample for 0.5 h at a temperature of 300°C:

$$K_s = \frac{\Delta m}{m} \times 100\%.$$

The porosity of the self-purifying coating was estimated based on its water absorption, which was found from the relative weight increase of the sample after immersion in distilled water for 2 h. The optimum interval for the formation of a catalytic coating was identified in an SNOL muffle furnace by monitoring simultaneously the porosity (based on water absorption) and the self-purification coefficient. The hardness of the coating was determined on a TML pendulum instrument according to GOST 5223–89, and the macrostructure on a MIN-4 microscope. The softening start temperature and the TCLE of the vitreous binder in a temperature interval of 20 – 400°C was measured on a DKV-3 vertical quartz dilatometer designed at the State Institute of Glass (GIS). The sintering temperature of the vitreous binder was identified based on the minimum heat treatment temperature under which the glass powder (particle size below 80 μm) deposited on a steel surface became resistant to abrasion.

The technological conditions of the formation of self-purifying catalytic coatings depend primarily on the thermal properties of glass binders 23f and 99 synthesized at the Institute of General and Inorganic Chemistry of the National Academy of Sciences of Belarus (Table 1). The properties of industrially produced undercoat enamel 2 are given as well for reference purposes.

TABLE 1

Vitreous binder	Properties of vitreous binder		Coating	Properties of coating	
	softening start temperature, °C	sintering temperature, °C		formation temperature interval, °C	self-purification coefficient, %
23f	420	540	23f-11	560 – 580	96
99	480	640	99-6	670 – 690	94
2	525	620	2-6	560 – 650	92

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Coating 23f-11 in a temperature interval of 560 – 580°C has sufficient strength, water absorption of 26 – 28%, and self-purification coefficient equal to 96%. After heat treatment at 600°C the porosity of the coating sharply decreases due to an increased quantity of the liquid phase, fusion symptoms (spotty luster) emerge on the surface, and the self-purification coefficient decreases to 60 – 65%.

It can be seen from Fig. 1 that as the temperature of heat treatment of coating 23f-11 grows from 540 to 600°C, the close-pored homogeneous structure transforms into a less ordered one and the linear sizes of the spherical and especially of the channel-shaped cavities grow. At a temperature of 520 – 540°C the coating has low mechanical strength (hardness), which is equal to 0.5 – 0.6 relative units (TML pendulum instrument) at the optimum formation temperature of 560 – 580°C. At a temperature of 600°C the coating swells, which leads to opening of pores and large-diameter craters that impair the coating strength.

Coating 99-6 with a self-purification coefficient of 94% is formed at a temperature of 670 – 690°C (exposure time 4 min). Within the interval of smooth spreading of the vitreous binder 99 (700°C) the porosity of the coating sharply decreases and the liquid phase envelopes the surface of the catalytic filler particles, which reduces the access of fat to the catalyst, as a consequence of which the self-purification coefficient decreases by 30%.

Figure 2 shows a photo of the cross-section of coating 99-6 at the optimum temperature of formation (680°C). The undercoat thickness is 0.28 mm, and the thickness of the self-purifying coating is 0.55 mm. The boundary between the undercoat and the self-purifying coat exhibits mutual penetration of the layers, i.e., the required adhesion is present. The outer surface of the coating is uneven and rough; pores and channels that reach the surface are visible. Such macrostructure provides for the optimum coefficient of self-purification in the coating: 94%.

The upper bound of the coating formation temperature is 30 – 40°C higher than the sintering temperature of the vitreous binder, which is 540°C for glass binder 23f, 620°C for glass binder 2, and 640°C for glass binder 99. The narrower the sintering interval of the glass binder, which we determine from the difference between the softening start temperature and the sintering temperature, the wider is the interval of formation of a porous coating. It can be seen from the data in Table 1 that the shortest sintering interval (95°C) is registered in vitreous binder 2, which provides for preservation of the volume of pores and channels of different linear sizes in a wider temperature interval. This ensures better technological

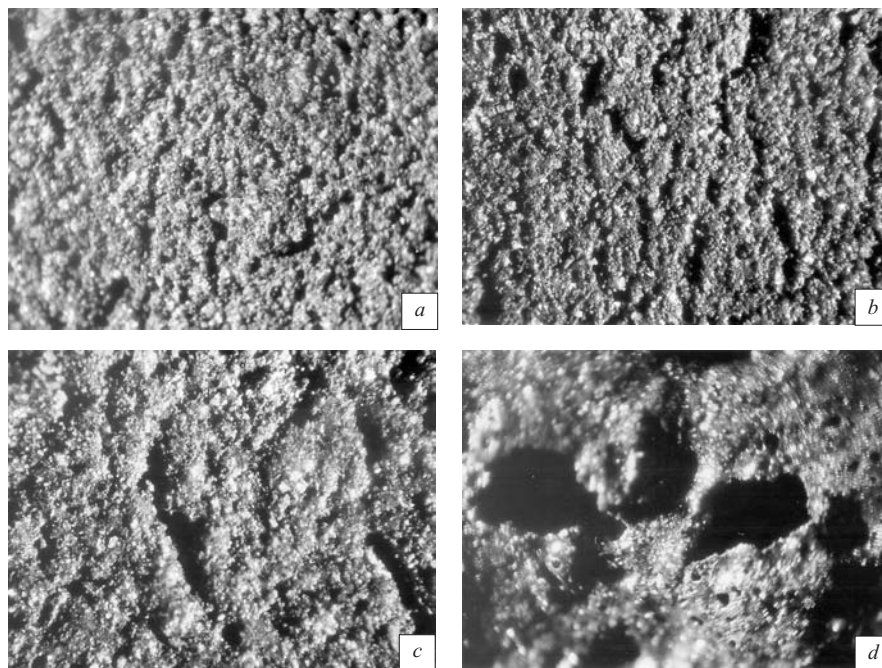


Fig. 1. Variation of macrostructure of self-purifying coating 23f-11 depending on temperature ($\times 55.5$): *a, b, c, and d*) temperature of 540, 560, 580, and 600°C, respectively.

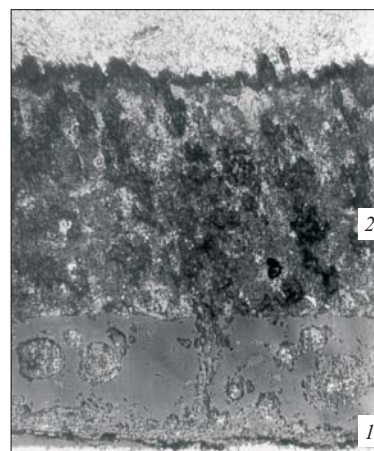


Fig. 2. Macrostructure of self-purifying coating 99-6 (cross-section, $\times 100$): *1*) undercoat enamel; *2*) self-purifying coating.

properties of the coating. Apparently, the specified interval can serve as a sintering rate characteristic (under isothermic exposure of 4 min) and the depth of structure variation in a thermally treated coating [2].

The effect of the degree of dispersion of vitreous binder 23f and the coating formation temperature on its quality and self-purification coefficient was studied as well.

A satisfactory quality of coating with good adhesion to undercoat enamel was obtained within a temperature interval of 560 – 580°C using a fraction of glass binder 23f from 60 to 80 μm . When the glass binder grain size ranges from 80 to 200 μm (heat treatment temperature 560°C), the degree of

TABLE 2

Coating	Water glass content, parts by weight	Firing temperature, °C	Hardness, rel. units	Water absorption, %	Self-purification coefficient, %
23f-9	8	560	0.30	—	93.3
		580	0.55	22	94.0
23f-10	10	560	0.46	—	94.8
		580	0.60	26	96.2
23f-11	12	560	0.53	—	96.0
		580	0.65	28	98.0
23f-12	14	560	0.55	—	98.3
		580	0.64	30	98.6

sintering is reduced and, consequently, the coating has low mechanical strength and adhesion of the self-purifying coating to the undercoat enamel. The presence of relatively large glass binder particles (60–80 μm) in the coating and fine particles of catalytic additives with grain size of 50–30 μm creates favorable conditions for making the porous structure coarser.

An increase in the concentration of sodium silicate solution (water glass: density 1.47 g/cm³, dry residue 41.8% according to GOST 13078–81) in the coating slip has a perceptible effect on the pore structure formation in self-purifying composite coatings that have a high content of finely dispersed filler.

It can be seen from Table 2 that as the water glass content grows from 8 to 14 parts by weight, the hardness of a coating fired at 560°C grows from 0.30 to 0.55, and that fired at 580°C up to 0.60. At the same time, water absorption of the coating grows from 22 to 30%, which is evidence of a more extended porous structure.

Thermocyclic testing of the self-purifying capacity of the coating (10 cycles of heating up to 300°C, exposure for 30 min, deposition of new drops after each thermostatic control) showed (Fig. 3) that introduction of 12 parts by weight

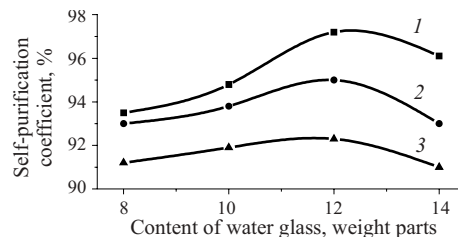


Fig. 3. The effect of water glass content in slip on the self-purification coefficient of coating based on glass binder 23f in thermocycling testing: 1, 2, 3 are the first, fifth, and tenth thermostatic cycles at 300°C, respectively.

of water glass into the slip is optimal, since a higher concentration has virtually no effect either on the coating hardness (Table 2), or on its self-purification coefficient. The decrease in the self-purification coefficient in thermal cycling is insignificant and remains over 92% after 10 treatment cycles, which indicates a stable performance of the self-purifying coating 23f-11.

Thus, it is established that the temperature interval for the formation of self-purifying coatings depends on the temperatures of softening and sintering of the vitreous binder, as well as on its dispersion. The most porous coating with a maximum self-purification coefficient (96–98%) was obtained on introducing 12–14 parts by weight of water glass into the slip.

The optimum structure of the coating provides for effective decomposition of food fats after multiple thermal cycles.

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